PHYSICAL PROPERTY MODIFICATION OF NANOTUBES

Cross-Reference to Related Applications

The instant application claims priority to U.S. Provisional Application Serial No. 60/064,539 filed 5 November 1997, the disclosure of which is incorporated by reference herein in its entirety.

Field of the Invention

The invention relates to processes involving nanotubes, and more specifically processes which are able to modify the physical properties of the nanotubes.

Background of the Invention

Carbon nanotubes are known as elongated tubular bodies which are typically only a few atoms in circumference. Methods of forming carbon nanotubes are described, for example, in U.S. Patent Nos. 5,753,088 and 5,482,601. The nanotubes are hollow and have a linear fullerene structure. Advantageously, the length of the nanotubes potentially may be millions of times

greater than the molecular-sized diameter. Carbon nanotubes are currently being proposed for a number of applications since they possess a very desirable and unique combination of physical properties relating to, for example, strength and weight. The nanotubes have also demonstrated electrical conductivity. See Yakobson, B.I., et al., *American Scientist*, **85**, (1997), 324-337; and Dresselhaus, M.S., et al., *Science of Fullerenes and Carbon Nanotubes*, 1996, San Diego: Academic Press, pp. 902-905. Investigative efforts regarding nanotubes have primarily focused on theoretical attempts to evaluate the nanotube molecular structure, and its potential relationship to physical properties.

Notwithstanding these efforts, there remains a need in art for a method to alter the physical properties of a nanotube such that it may be modified for various end use applications. For example, it would be particularly desirable to be able to alter the electrical properties within the nanotube such that the nanotube exhibits heterogeneous electrical behavior. As a result, the nanotube may be useful in microelectronic device applications which often demand high thermal conductivity, small dimensions, and light weight.

Summary of the Invention

It is therefore an object of the invention to provide a method of modifying a physical property of a nanotube, such as an electrical property.

It is a further object of the invention to provide a nanotube having modified physical properties.

These and other objects and advantages are provide by the present invention. In one aspect, the invention provides a method of modifying a physical property of a nanotube. The method comprises subjecting a nanotube having a defined lattice structure orientation to stress conditions sufficient to disrupt the lattice structure orientation. A dipole of dislocation cores is formed therein, and the dipole of dislocation cores split and propagate in the nanotube in a manner such that the dipole of dislocation cores is separated by at least one domain of

modified structure. As a result, at least one physical property of the nanotube is altered.

In one embodiment, the above method also includes exposing the nanotube to thermal conditions. In another embodiment, the method of the invention also includes the step of exposing the nanotube to radiation, preferably in the form of ultraviolet light or x-ray.

In a typical embodiment, the nanotube initially has a hexagonal core lattice structure and the application of stress disrupts this core lattice structure to form a dipole of pentagon-heptagon and heptagon-pentagon dislocation cores in the nanotube. These dislocation cores propagate throughout the nanotube such that a domain of modified lattice structure is formed between the dipole of dislocation cores as described herein.

In another aspect, the invention relates to a nanotube comprising: (1) a dipole of pentagon-heptagon dislocation cores located in an opposed spaced-apart relationship along a longitudinal axis of the nanotube; (2) a first region comprising a domain of modified lattice structure positioned between the dipole and formed by the dipole propagating throughout the nanotube as a result of stress being applied to the nanotube; and (3) second and third regions each positioned on opposite sides relative to the first region, the second and third regions comprising lattice structure domains which differ from the domain of modified lattice structure present in the first region such that the second and third regions possess a physical property different from the first region.

Brief Description of the Drawings

FIG. 1 illustrates a nanotube having a hexagonal core lattice structure;

FIG. 2a illustrates a dipole of dislocation cores formed in the nanotube described in **FIG. 1**;

FIGS. 2b and **2c** illustrates the propagation of the dipole of dislocation cores in the nanotube;

FIG. 3 illustrates a nanotube having an altered lattice structure;

FIG. 4 illustrates a nanotube having multiple dipoles of dislocation cores formed therein; and

FIG. 5 illustrates a configuration of multiple concentric nanotubes.

Detailed Description of the Preferred Embodiments

The invention will now be described in greater detail with reference to the accompanying drawings and embodiments set forth in this section of the application. It is to be understood, however, that these embodiments are for illustrative purposes only, and do not in any way limit the scope of the invention which is defined by the claims.

In one aspect, the invention relates to a method of modifying one or more physical properties of a nanotube. Examples of physical properties which may be modified include, for example, mechanical and electrical properties. The method comprises subjecting a nanotube having a defined lattice structure orientation to stress conditions sufficient to disrupt the lattice structure and form a dipole of dislocation cores therein. The dipole of dislocation cores split and propagate in the nanotube in a manner such that the dislocation cores are separated by at least one domain of modified structure, and wherein at least one physical property of the nanotube is altered. As described in greater detail herein, the chirality, or more specifically helicity, of the nanotube is altered during the method of the invention. In particular, the domain of modified lattice structure located between the dipole of dislocation cores experiences a transformation in chirality. For the purposes of the invention, the term "chirality" may be defined as a corkscrew symmetry of the nanotube, specified, for example, by the angle between the nanotube circumference and the zig-zag motif in the honeycomb atomic structure of the nanotube wall. The chirality may also be defined as a pair of integers (c_1,c_2) marking the circumference of the nanotube in a standard basis for a hexagonal lattice, wherein c_1 and c_2 may each individually range from 0 to 30, provided that both c_1 and c_2 may not simultaneously be 0.

For the purposes of the invention, a "nanotube" is defined conventionally, and is a tubular, strand-like structure which has a circumference on the atomic scale. The typical diameter of a nanotube ranges from about 1 nm to about 10 nm. The nanotube may be formed from various materials such as, for example, carbon, boron nitride, and composites thereof. The nanotube typically is formed from carbon. In such an embodiment, the nanotube is formed as a fullerene molecule containing a hexagonal lattice structure. Methods for making carbon nanotubes are known in the art, and are described, for example, in U.S. Patent Nos. 5,753,088 to Olk and 5,482,601 to Ohshima et al., the disclosures of which are incorporated herein by reference in their entirety.

The stress applied to the nanotube is typically carried out using conventional equipment. For the purposes of the invention, a magnitude of stress is typically applied such that the nanotube lattice structure is altered or disrupted as set forth herein, with the nanotube elongating preferably from about 1 to about 15 percent, and more preferably from about 3 to about 8 percent. The stress may be applied to the nanotube in various forms like, for example, tensile stress, torsional stress, bending stress, and combinations of the above. The magnitude of the applied stress preferably ranges from about 30 MPa to about 80 MPa.

The method of the invention may take place over various periods of time. Preferably, the method is carried out from about 1 min to about 180 min.

The method of the invention may also include other types of processing to alter one or more physical properties of the nanotube. For example, the method may further comprise subjecting (e.g., exposing) the nanotube to thermal conditions (i.e., heat) using conventional techniques. In this embodiment, the temperature to which the nanotube is exposed preferably ranges from about 500°C to about 1800°C. If so desired, the nanotube may be further subjected (e.g., exposed) to radiation, preferably ultraviolet radiation, x-ray radiation, or combinations thereof.

The method of the invention will now be described in greater detail with reference to the drawings. **FIG. 1** illustrates a carbon nanotube **10** having a lattice structure orientation represented by the chirality vector (10,10). The nanotube **10** may be characterized by having a virtually defect-free lattice structure as represented by the hexagonal cores **20** in **FIG.1**. Force is then applied to the nanotube **10** in the manner described herein. Although not wishing to be bound by any theories, it is believed that an initial slip in the lattice structure occurs by rotating a bond in the lattice structure, typically a lattice bond originally orientated along the circumference **c** of the nanotube, such as a dipole that is represented by a vector ± (0,1). Equivalently, a similar degeneracy may take place for a dipole that is ± (1,0). The above physical phenomena is described in detail in Provisional Application Serial No. 60/064,539 filed 5 November 1997.

As a result of the application of stress, a dislocation dipole **30** is formed in the nanotube as shown in **FIG. 2a.** For the purposes of the invention, the term "dislocation dipole" is defined as a pair of lattice structures formed in the nanotube as a result of the application of stress which are distinguishable from the lattice structure of the nanotube prior to application of stress. In this illustrated embodiment, the dislocation dipole has a pentagon-heptagon (5-7) **30a** and heptagon-pentagon (7-5) **30b** lattice structure. As force continues to be applied to the nanotube **10**, the dislocation dipole **30** propagates in opposed directions from a reference point **x** in the nanotube, thus gilding along a spiral "slip plane". The dipole propagation is depicted in **FIG. 2b** and **2c,** as well as **FIG. 3** which illustrates a spiral path of propagation **p** for the dipoles **30a** and **30b** relative to the longitudinal axis **l** of the nanotube **10'**. As illustrated, stress is applied axially to the nanotube as denoted by the opposing arrows in **FIG. 3**. During the propagation, the region between the propagating dipole **30a** and **30b** evolves into a new lattice structure, namely one comprised of hexagons (depicted by **30c**) having a orientation different (i.e., by 2 degrees) from the initial hexagonal structure referred to above. Expressed differently, a (10,10) nanotube having a chiral angle of x=30° for a (10,10) nanotube changes to a chiral angle of x=28° for a (10,9) nanotube which has a modified hexagonal

lattice structure. Thus, the chirality (i.e., helicity) of the domain of modified lattice structure **30c** undergoes a transformation, and at least one electrical property of the domain of modified lattice structure is altered. Using the example of a nanotube having an initial chirality vector of (10,10), the chirality of the domain of modified lattice structure becomes (10,9). The lattice structure having the (10,10) vector is metallic, and may have an electrical resistivity ranging from about 10^{-6} Ωcm to about 10^{-4} Ωcm. The domain of modified lattice structure, in this example, is characterized in having a (10,9) vector and is considered to be a semiconductor having an energy band gap ranging from about 0.5 eV to about 1.5 eV (electron-volts).

As a result of the method of the invention, the nanotube **10** elongates and the diameter changes in a step-wise fashion ($\mathbf{d_1}$ to $\mathbf{d_2}$) which is illustrated in **FIG. 3**. As shown by **FIG. 3**, a first region **50** is present in the resulting nanotube **10'** and comprises a domain of modified lattice structure as described herein (see **30c** in FIGS. **2b** and **2c**) positioned between the dipole of dislocation pairs **30a** and **30b**. The first region **50** is formed by the dipole propagating throughout the nanotube as a result of stress being applied to the nanotube. Second and third lattice structure regions, **40** and **60** respectively, are positioned adjacent to each of the dislocation structures **30a** and **30b** and opposite to the first region **50**. The second **40** and third **60** regions of the nanotube **10'** possess lattice structures that are different from the first region **50** such that the physical properties of the second and third regions differ from those in the first region **50**.

Typically, the second and third regions have the hexagonal lattice structure similar, and in most cases identical, to unstressed structure of the nanotube, and thus have similar lattice structures. It should be appreciated, however, that for the purposes of the invention, the second and third regions may have different lattice structures.

When the dislocation dipole propagates (i.e., glides) away in opposed directions along the longitudinal axis **l** of the nanotube **10**, at least one other dislocation dipole may be formed in the nanotube and thus may further narrow the diameter of the elongated nanotube and increase its elongation of the tube.

Thus, a nanotube **10''** having multiple diameters (d_3 through d_5) may be formed as illustrated in **FIG. 4**. The nanotube **10''** contains various regions which may have different lattice structures. More particularly, the lattice structures of these regions may vary in terms of minimum energy band gap from 0 (metal) to a very large number such that the region(s) are not electrically conductive. A chirality vector illustrating the formation and propagation of multiple dislocation core dipoles may be illustrated as follows for a (10,10) nanotube:

(10,10) ⟶ (10,9) ⟶ (10,8) ⟶ ..... ⟶ (10,0) ⟶
[(9,1) *or* (10,-1)] ⟶ (9,0) ⟶ [(8,1) *or* (9,-1)] ⟶
(8,0) ⟶ [(7,1) *or* (8,-1)] ⟶ (7,0) *etc.*

The nanotube **10** may be used in conjunction with multiple nanotubes (**80** and **70**) of differing diameters such that the nanotubes form a layered concentric structure as illustrated in **FIG. 5**.

In general, the nanotubes of the invention are advantageous in that they may be incorporated into various articles of manufacture such as, but not limited to, infrared sensors for thermal imaging, nanoscale diodes, photoelectric cells, (molecular) nanoscale transistors for submicroelectric devices.

Employing the method of the invention, the nanotubes may be present as heterojunctions, and accordingly are desirable for use as integrated circuit devices which require high radiation resistance, light weight, and thermal stability.

In yet another aspect, the invention relates to a method of altering the chemical functionality of a nanotube. The method includes providing a nanotube having dislocation cores (as defined above) formed therein and a reactive component. The reactive component may be selected from various components containing chemically reactive substituents such as, but not limited to, hydroxy,

carboxy, amino, and the like, as well as specific ligands for protein binding. The reactive component, namely the chemically reactive substituents, react with the dislocation cores such that the chemical functionality of the nanotube is altered. This method may be carried out using known techniques and equipment.

The nanotube having chemically altered functionality is useful in that it may be useful in a variety of end use applications that may require such a modified structure. Examples of end use applications include, but are not limited to, chemical sensors for local environment characterization, intracellular nanoprobes for biological and medical studies, and medical connects/bridges between other molecules or particles.

Disclosed herein are specific preferred embodiments as described by the above specification and accompanying drawings. It should be appreciated, however, that this disclosure is only meant to illustrate the invention, with the scope of the invention being defined by the claims.